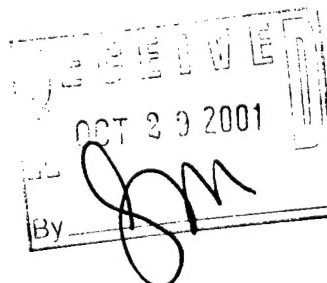


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13. ABSTRACT (Maximum 200 words) Langmuir films of novel amphiphiles that present reversible collapse and two immiscible liquid phases are reported. The amphiphiles are distinguished by very large "bulge" groups that are significantly larger than the amphiphile chain. Brewster Angle Microscopy studies and absorption isotherms are used to demonstrate these findings. A major theoretical advance is reported using a solid state approach through mean field theory to model all observed solid like phases of Langmuir films of alkanolic acids or alcohols. Adaptation of the model amphiphiles to form molecules for formation of self-assembled monolayers with controlled frictional properties was unsuccessful.		
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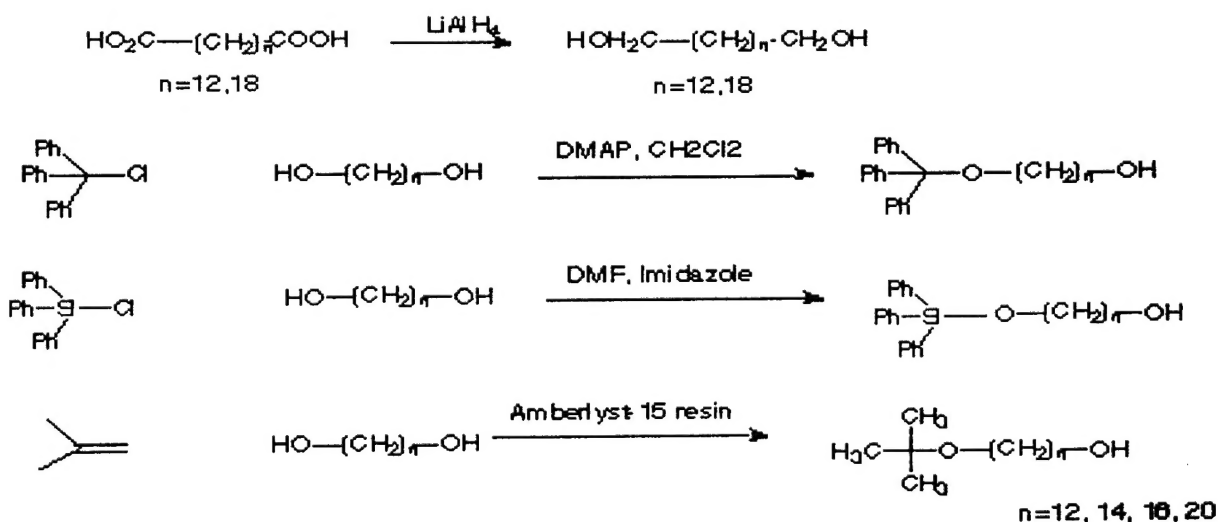
1. Statement of the problem studied

The object of this research was to produce monolayer films, preferably as self-assembled monolayers, that would have unique frictional properties. The films would have large groups at the end of amphiphilic chains that would form molecular "cups" or "grooves" that would accommodate fullerenes so that the surface would become one of "molecular ball bearings." Another goal was the production of amphiphiles that could produce ferroelectric monolayers. The research was on three fronts: synthetic, physical measurements and theoretical. Of course, the critical part was in the production of successful amphiphiles that would provide the material for formation of the monolayers. The separate aspects of the research will be treated separately.

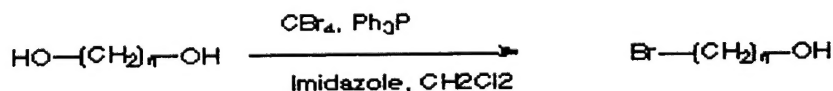
2. Summary of most important results

2.1 Summary of synthetic results

Ball and Stick Amphiphiles: Etheral Linkage

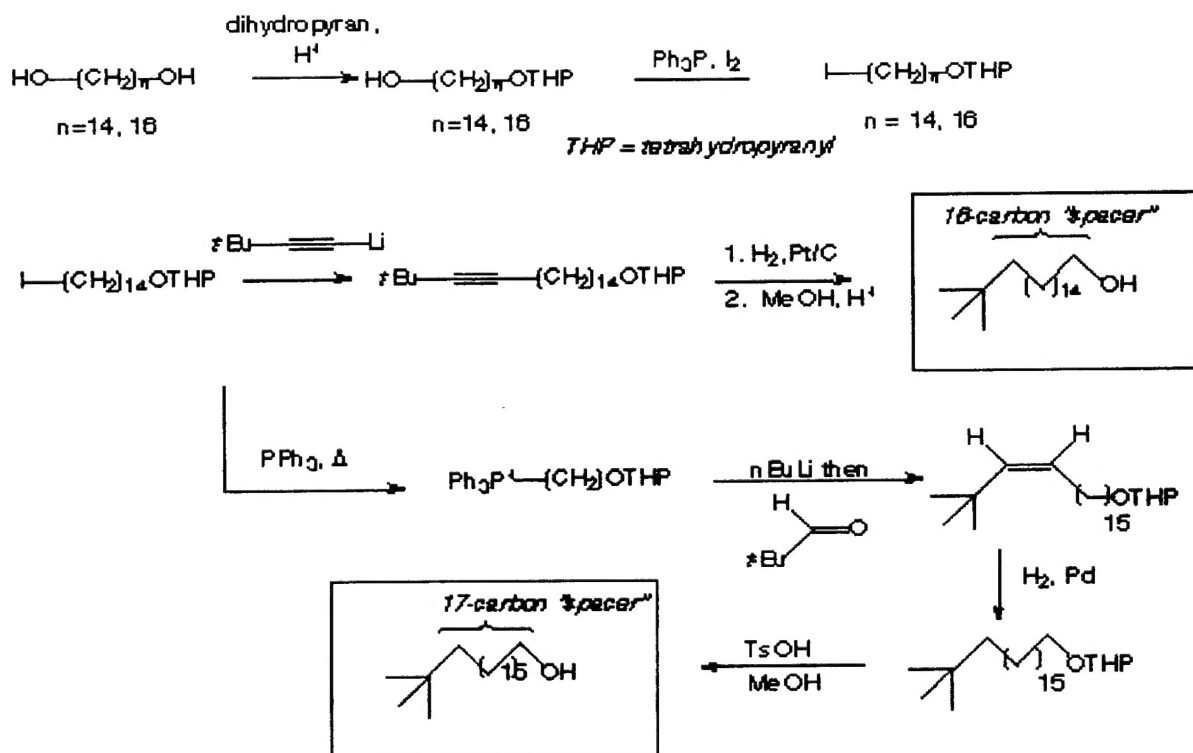


Brominated Terminus



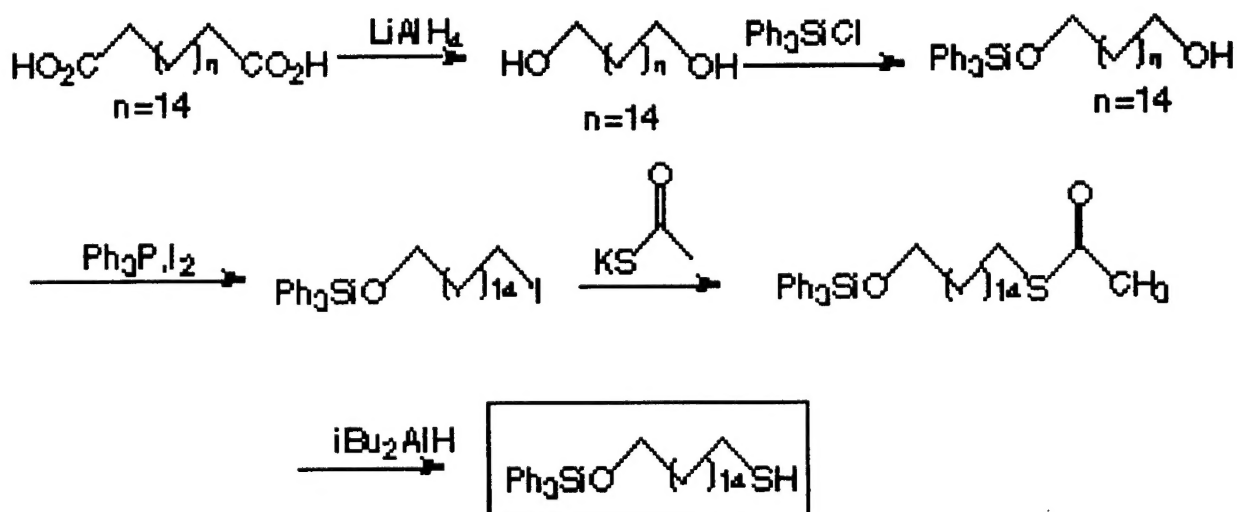
The synthetic goal was to create a new class of amphiphiles with capability to form monolayers, particularly self-assembled ones, with tribological and ferroelectric properties. These molecules contain large hydrophobic binding surfaces connected via a nonpolar linker to a typical LB (alcohol) or SAM (thiol) head group. Initial efforts in this class involved monoalkylation of long-chain diols with triphenylsilyl and triphenylmethyl halides to form "ball and stick" amphiphiles in which the triphenylsilyl or triphenylmethylethers formed the "ball"; the choice of the diol determined the length of the "stick". Initial LB results found members of this class to have a unusual and virtually unprecedented phase behavior in which compression resulted in a completely reversible formation of

Ball and Stick Amphiphiles with all-Carbon Backbone:
t-Butyl hexadecanol and t-Butyl heptadecanol



a somewhat ordered liquid-phase. Realizing that the properties of these phases were not only a new phenomenon but might hold significant implications for molecular level tribology, a number of "ball and stick" systems in which the size of the ball was varied from trimethylmethyl (tert-butyl) to

Synthesis of ball and stick thiols



triphenylmethyl (trityl) to triphenylsilyl, while the size of the stick was varied from twelve to twenty carbons. The tert-butyl analogs were prepared by acid-catalyzed addition of an alcohol across the double bond of isobutylene. A number of the requisite diols were not commercially available and were prepared by reduction of diacids.

The synthetically efficient preparation of the initial amphiphiles left, as a residue, electronically polar ether oxygen. These ether oxygen atoms, by virtue of position within the molecules, were expected pack within the otherwise hydrophobic portion of the LB films. Although the ether oxygens were to some degree shielded or "hidden" by the steric bulk of the neighboring tert-butyl, triphenylmethyl, or triphenylsilyl groups, it was a question what effect the presence or absence of these ethers would have on the unusual phase behavior. Syntheses of "all carbon ball and stick" amphiphiles in which the ether oxygen was replaced by a methylene CH_2 was undertaken. In addition, to investigate whether the effect varied with odd- or even chain lengths, methylene backbone analogs were prepared containing both sixteen and seventeen CH_2 spacers between the tert-butyl tail and the alcohol head group.

Finally, a preparation of analogs of the ball-and-stick amphiphiles was sought which would be useful for incorporation into self-assembled monolayers. This involved an overall similar route as employed for synthesis of the amphiphiles above except that the "head group" alcohol was converted to a leaving group to facilitate introduction of a thiol as the stable thioacetate ester. A successful approach to this preparation was not found within the time-frame of the funded research period

2.2 Summary of physical measurements

The unique amphiphiles studied were characterized by very large groups at the end of the aliphatic chain, cap groups. The films exhibited very unusual isotherms that exhibited common behaviors: (1) reversible collapse, (2) great fluidity, (3) unique liquid-expanded phase behavior. Although the details of the behavior varied according to the chain length, the type of cap group, and the cap group attaching atom, C or Si, the general behavior was distinctive. The films did not produce particularly high surface pressures and never reached a solid phase behavior. Thus it was not possible to have films that transferred reliably to solid subphases for study by atomic force microscopy (AFM) or to make frictional or ferroelectric films. However, the phase behavior was sufficiently interesting to pursue while attempts to synthesize amphiphiles that formed stable solid phases could be executed.

The reversible collapse is seen in the surface isotherms by the system retracing the surface isotherm after it has traversed an apparent critical collapse point. This remarkable behavior was general with all of the amphiphiles studied and apparently is a function of the significantly larger cross section of the cap group compared to that of the aliphatic chain. Brewster angle microscopy (BAM) shows the film to be perfectly homogeneous before collapse except there are always a few regions where there is a circular area of equivalent brightness to the rest of the film but it is bordered by a somewhat different brightness of that resembles a scar. At the collapse point the film image exhibits small bright mostly circular regions that "bloom" at the apparent collapse pressure and becoming increasingly dense thereafter. Upon release of surface pressure the images more or less reverse their pattern with the film becoming homogeneous once again after the apparent collapse pressure is passed. This pattern of images can be repeated for tens of cycles with no apparent change in behavior as long as the pressure reversal is initiated at surface areas that are not more than 20% less than the apparent collapse area.

Similar behavior was reported by Schroeter et al. who were examining amphiphiles that had very large semi-planar groups attached to the polar head and that had aliphatic chains attached to the large groups; essentially they had "cap" groups at the base of the aliphatic chain rather where it attaches to the polar head than at its terminus. Their hypothesis is that a trilayer is formed but there are several difficulties with this model.

If the barriers on the trough were decreased to yield exceptionally small areas per molecule, irreversibility of the surface isotherm would be observed on opening the barriers. While the reversible behavior is somewhat dependent on barrier closing rate, it is not significant. The geometry of the instrument did not allow BAM observations at these small areas. Some of the amphiphiles display another rise upon increasing the surface pressure beyond the collapse point with a subsequent collapse point being observed at higher surface pressure than the first and at significantly smaller molecular area. This collapse is followed by another plateau. Reversibility after the second collapse was also observed. Also, the slope of the rise from the first plateau following the first apparent collapse pressure was always less than that of the rise to the first apparent collapse point.

Exceptional behavior common to these amphiphiles was also observed in the region of very low surface pressures ≤ 4 mN/m and concomitantly large effective molecular areas. In this case the unusual behavior is seen in BAM images. In what appears to be a liquid-expanded region, the monolayer exhibits significant flow activity with "pools" of the amphiphile showing "bubble" moving, in highly directional fashion, through them. The unusual behavior is observed when increased surface pressure leads to an image that is bright and largely homogeneous. However, this film has dark, mostly circular dark zones. It might be thought these are pockets of the aqueous subphase but they are not. Close examination shows some have very small bright circles inside. Because the films are dynamic they are in constant motion under the light beam of the BAM. If these bright dots were freely floating bits in an open aqueous region of the film, they would collect against the edge of that region that trails the flow direction. Instead they move at the same relative rate as the surrounding bright film, i.e. they are entrained inside of the dark region. Thus the dark region must be another form of the amphiphile. It is clear from the flow behavior, low surface pressure, and very large average molecular area, and darkness of the region, that the entraining material cannot be a solid-like phase. It is clear that the bright phase at these surface pressures, given the ease of propagation of "bubbles" through it and its ease of flow, must be a liquid phase also. Thus, we are left with the remarkable observation that *we are observing two immiscible liquids of the same pure material!* However, it is not at all certain that the two liquids are in thermodynamic equilibrium although the images persist for hours.

Observation made upon further expansion of these immiscible liquid films with smaller quantities of material giving lower surface coverage exhibits no palpable surface pressure. However, BAM indicates that there are dark regions that float by that are not, however, as black as most of the image which should be, because of low coverage, water. Further, expansion of the film formed from compression at this low coverage shows that little pieces of film image as if they were remnants of the interfaces between the two liquids. This indicates that the two liquids are made immiscible from a very large line tension that separates them. This line tension is so strong, in fact, that while the matter of the two films it separates is dispersed, the line tension structure is retained and seen in the BAM images!

A major conclusion of our theoretical work is that Langmuir monolayers of paraffinic amphiphiles, and by extension any amphiphile of reasonably regular cross section, that displays typical Langmuir monolayer behavior, should be treated as two-dimensional solids rather than as hexatic

(liquid-crystalline) phases. It is clear that these amphiphiles do not conform to the prototypical fatty acid film behavior.

The fold-over mechanism of Schroeter and coworkers cannot explain the behavior of these amphiphiles since it cannot rationalize the second apparent collapse we observe. Our model for these systems is, that in contrast to most Langmuir films that exhibit typical gas-liquid-solid phase behavior, they are truly liquid-crystalline two dimensional phases. This model can best be followed by beginning with the film at near zero surface pressures and very large average molecular areas. In the 2D gas phase, the amphiphiles at low coverage are far apart and most lying horizontally. Actually arenes and aliphatics have a finite solubility in water and, at these coverages, this disposition is not unreasonable. As the barriers are closed many of the amphiphiles come together and rise from the water depending on local environment. However, some of these are trapped in the horizontal position and become irreversibly entrained with some of the large head groups caught between the chains of standing amphiphiles. As surface pressure increases most of the amphiphiles are standing out of water but areas of horizontal ones are caught in pockets which are essentially buttressed by the very strong line tension formed by the intertwined horizontal/vertical amphiphiles. Apparently, this can be so severe that the line interfaces cannot disentangle even when the film is re-expanded to the gas phase as evidenced by the observation of floating pieces of line interfaces.

Upon further increase of pressure the film becomes homogeneous and at sufficiently high pressures the line interfaces deform to be mostly vertical and thus force the interior horizontal amphiphiles to rise out of the water in either a tilted or vertical arrangement. This phase is still fairly fluid and, because of this, it is thought to be a smectic-like (hexatic) monolayer than one possessed of close packed solid-like character.

At the apparent collapse, the pressure is sufficient to force aggregates of the amphiphiles out of the plane. It is this that leads to the appearance of the bright spots in the BAM image. The structure is then like a nematic with all of the amphiphiles more or less vertical but at different heights - some squeezed out of the monolayer probably because of unfavorable disposition of their cap groups. These are probably more like domains that get squeezed out by other domains and, in this way, are not exactly like a nematic because the vertical disorder is not entirely random. This arrangement explains reversible collapse for when the surface pressure is released, the clusters forced out of the smectic phase are free to "drop" back onto the aqueous subphase. The process is reversible because none of the regions are forced out so far that they are trapped on the surface of the monolayer such as occurs in the collapse of alkanoic amphiphiles.

The second rise and plateau can be rationalized but, unfortunately, without any BAM images to assist. The change of slope on the rise, however, indicates that the phase formed is actually melting under the increase of pressure. This is entirely consistent with liquid crystal behavior in that the sequence smectic-nematic-liquid can occur on increase of temperature and may also be expected to increase with pressure if the situation is akin to the water phase diagram liquid/solid equilibrium line. Now the reversibility is between the amphiphile liquid, although probably a fairly anisotropic one with a director more or less normal to the subphase plane, and nematic phase. It is easily envisaged how release of pressure on the liquid would cause it to form the nematic monolayer phase. Another viewpoint is that the second apparent collapse pressure marks the point at which the nematic monolayer is extruded into a nematic multilayer.

This model provides a consistent description of the behavior of these films. Their inability to form 2D solids is a result of the disparity in size of the cap group and the chain and head groups. The efficient packing required by a solid cannot be achieved and, as in the case of mesogens, intermediate

phases, essentially a 2D smectic and nematic, are formed. To our knowledge, this is the first report of such observations and model.

2.3 . Summary of theoretical results

The theoretical arm of this research was to model and explain the new phenomena that were expected for the tribological and ferroelectric monolayers. However, to understand such behavior, it was felt necessary to describe the behavior of standard fatty acid amphiphiles. This led to the first theory that accounts for all the observed phases (except liquid and gas) of fatty acid/alcohol amphiphiles.

The model is based on a rigid hexagonal lattice formed by the polar head groups. The aliphatic tails are then allowed to move freely and using spherical harmonics as order parameters, a complete mean field theory, common to that used for the solid state, is developed that is based on the symmetries of these functions. By use of symmetry breaking principles akin to those employed in the mean field theory of solid state phase transitions, results consistent with all reported phase behavior of Langmuir monolayers.

The theoretical development has been able to show that amphiphiles may be represented as elastic multipoles and that this approach can be adapted to modeling films that have dopants or defects. Viewing the monolayer as an elastic medium renders its theoretical treatment straightforward.

This approach opposes the long-held concept of fatty acid Langmuir monolayers as mesophases possessing the hexatic behavior required of such systems. However, Langmuir monolayers are not truly two-dimensional and the concept of hexatic structure valid only in strictly two-dimensional systems. Thus, the generality and easy adaptability of the solid state approach to Langmuir monolayers offers a more flexible formalism and realistic model of film behavior.

This theoretical work has received recognition and a major review of it was invited as a chapter in the Handbook of Thin Film Materials which is to be published in late 2001.

3.0 Publications

Book Chapter:

A solid-state approach to Langmuir monolayers, their phases, phase transitions, and design. Eckhardt, Craig J.; Luty, Tadeusz in "Handbook of Thin Film Materials", H. S. Nalwa, ed. (Academic Press, San Diego, (2002) Pp. 685-733.

Publications in Peer Reviewed Journal:

Langmuir monolayers as disordered solids: Disorder and elastic fluctuations in mesophases. Luty, Tadeusz; Eckhardt, Craig J.; Lefebvre, Jacques. J. Chem. Phys. (1999), 111(22)

Langmuir monolayers as disordered solids: Strain-tilt-backbone coupling and natural order parameters for the swiveling transitions. Luty, Tadeusz; Swanson, David R.; Eckhardt, Craig J.. Department of Chemistry, J. Chem. Phys. (1999), 110(5), 2606-2611.

Langmuir monolayers as disordered solids: Strain-state calculations applied to stearic acid. Swanson, David R.; Luty, Tadeusz; Eckhardt, Craig J. J. Chem. Phys. (1997), 107(12), 4744-4750.

Model calculations of Langmuir monolayers: Pressure effects on tilting behavior of idealized amphiphiles. Swanson, D. R.; Hardy, R. J.; Eckhardt, C. J. *J. Chem. Phys.* (1996), 105(2), 673-677.

Papers Presented at Meetings but not Published in Conference Proceedings:

Unusual collapse behavior of a Langmuir film of a novel amphiphile. Flores, H.; Erickson, C. A.; Lech, A.; Hagen, J.; Eckhardt, C. J.. Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000 (2000).

Inventions: None

4.0 Those supported and receiving advanced degrees:

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